



Evaporation and diffusion behavior of fuel mixtures of gasoline and kerosene

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ABSTRACT

Kerosene is widely used in lamps and stoves and is less of a fire hazard than other fuels, such as mineral spirits, due to its flash point being above 40 °C and low vapor pressure at normal ambient temperatures. At room temperature and pressure, the concentration of vapor above a kerosene spill is well below the lower flammability limit, but gasoline addition to kerosene will increase the vapor pressure and the ignitability of kerosene. The aim of this paper is to accurately predict the evaporation and diffusion behavior of fuel mixtures of gasoline and kerosene in an arbitrary mixture ratio. While the vapor pressures of gasoline and kerosene, which are both multi-component liquid fuels, decrease with the progress of evaporation, it is demonstrated that the vapor pressures can be expressed by exponential functions of weight loss fractions. The vapor pressures, evaporation rates and flash points of gasoline/kerosene mixtures can be modeled accurately by treating them as two-component mixtures, using empirically-derived constants for each component, which this paper gives. Furthermore, a predictive model of a concentration distribution of vapor above a fuel mixture spill on a floor was derived. Ignition experiments of fuel vapor were carried out, and the model was experimentally verified. The method presented in this paper can provide useful information to estimate the fire hazard in scenarios where a fuel mixture of gasoline and kerosene in an arbitrary mixture ratio is spilt on a floor.

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1. Introduction

It is easy to obtain kerosene as well as gasoline, and both fuels are often used as an accelerant in arson. There is little or no difference in flame heights of pool fires between gasoline and kerosene [1]. On the other hand, kerosene has a vapor pressure much lower than that of gasoline and cannot form a flammable mixture in an ambient atmosphere at room temperature. In some arson cases, mixtures of gasoline and kerosene have been used as accelerants. Adding kerosene into gasoline decreases the vapor pressure and the vaporization rate, reducing the size of the area where a flammable mixture can be formed. These changes are expected to be very sensitive to the mixture ratio of gasoline and kerosene. We must accurately predict where a flammable mixture spreads, in order to estimate the fire hazard in case of liquid fuel spills [2]. Shepherd et al. discussed the change in flash points and vapor pressures of kerosene by gasoline contamination [3]. Fingas empirically demonstrated that most crude oil and petroleum products evaporate at a logarithmic rate with respect to time and presented a simple model for predicting the weight fraction evaporated as a function of temperature [4–6]. However, there have not been any previous reports of quantitative investigation of how much

fire hazard decreases by adding kerosene into gasoline or how much fire hazard increases by adding gasoline into kerosene.

In this work, fuel mixtures of gasoline and kerosene were used as samples, and the change in evaporation characteristics of these samples by evaporation and the time variation of a concentration distribution of vapor from a fuel mixture spill on a floor were measured. "Weight loss fraction" was chosen as the parameter signifying progress of evaporation. The weight loss fraction a is given by:

$$a = (w_0 - w)/w_0 \quad (1)$$

where w_0 is the initial weight of fuel mixture (kg) and w is the current weight of gasoline (kg). While gasoline and kerosene were multi-component liquid fuels, they were assumed to be a two-component liquid mixture of gasoline and kerosene, from which the evaporation model of fuel mixtures was derived. The change in concentration of fuel mixtures during evaporation was predicted by the model, and compared with the measured values. A diffusion model above a fuel mixture spill on a floor was prepared based on the unidimensional diffusion equation [7], and a method for predicting a concentration distribution of flammable vapor generated from a fuel mixture of gasoline and kerosene in an arbitrary mixture ratio will be presented. Furthermore, ignition experiments of fuel vapor were carried out and the test results were compared with the ignition prediction in order to verify the presented method.

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Nomenclature

a	weight loss fraction (-)	R	gas constant (8.314 J/molK)
a_g	weight loss fraction of gasoline (-)	S	evaporative area (m^2)
a_k	weight loss fraction of kerosene (-)	t	time (s)
C	concentration of fuel vapor (vol%)	t_i	ignition time (s)
$C_{0,t}$	concentration of fuel vapor on the surface of fuel mixture at time t (vol%)	T	temperature (K)
$C_{z,t}$	concentration of fuel vapor at time t and height z (vol%)	T_f	flash point (K)
d	thickness of fuel mixture spill (mm)	v	evaporation rate of fuel mixture ($\text{kg}/\text{m}^2\text{s}$)
D	diffusion constant of fuel vapor (m^2/s)	v_g	evaporation rate of gasoline component in fuel mixture ($\text{kg}/\text{m}^2\text{s}$)
h_i	ignition height (m)	v_k	evaporation rate of kerosene component in fuel mixture ($\text{kg}/\text{m}^2\text{s}$)
k	mass transfer coefficient (m/s)	w	current weight of fuel mixture (kg)
k_g	mass transfer coefficient of gasoline (m/s)	w_0	initial weight of fuel mixture (kg)
k_k	mass transfer coefficient of kerosene (m/s)	x_g	molar fraction of gasoline component in fuel mixture (-)
m, n	evaporation rate constant of fuel mixture (-)	x_k	molar fraction of kerosene component in fuel mixture (-)
M_g	molecular weight of gasoline (0.08 kg/mol)	X_{g0}	initial weight fraction of gasoline component in fuel mixture (-)
M_k	molecular weight of kerosene (0.12 kg/mol)	y_g	molar fraction of gasoline component in fuel vapor (-)
N_g	evaporative molar of gasoline in fuel vapor (mol)	y_k	molar fraction of kerosene component in fuel vapor (-)
N_k	evaporative molar of kerosene in fuel vapor (mol)	$\alpha_A, \alpha_B, \beta_A, \beta_B$	vapor pressure constant (-)
p	total vapor pressure of fuel mixture (Pa)	$\alpha_{A,g}, \alpha_{B,g}, \beta_{A,g}, \beta_{B,g}$	vapor pressure constant of gasoline (-)
p_0	atmospheric pressure (101,300 Pa)	$\alpha_{A,k}, \alpha_{B,k}, \beta_{A,k}, \beta_{B,k}$	vapor pressure constant of kerosene (-)
p_g	partial vapor pressure of gasoline component in fuel mixture (Pa)	θ	standardized time ($\text{m}^2\text{s}/\text{kg}$)
p_k	partial vapor pressure of kerosene component in fuel mixture (Pa)		

2. Experimental

2.1. Preparation of samples

Motor regular gasoline and kerosene, which were purchased at a gas station and were in conformity to JIS K 2202 and 2203, were mixed in weight ratios of two-to-one, one-to-one and one-to-two, and prepared the three kinds of fuel mixtures. These fuel mixtures are hereinafter called “2:1 fuel mixture”, “1:1 fuel mixture” and “1:2 fuel mixture”, respectively. Six degraded fuel mixtures with different weight loss fractions from 0 to 0.25 in increments of 0.05 were prepared by leaving the fuel mixtures in an open tray (the base area: 0.1 m^2) at 20 °C. Vapor pressures and flash points of seven samples including a virgin fuel mixture of each mixture ratio were measured.

2.2. Vapor pressure measurement

Vapor pressures of the degraded fuel mixtures were measured in the range from 10 up to 40 °C at the intervals of 5 °C using an automated vapor pressure tester (Tanaka Scientific Ltd. AVP-30D). A sample cylinder was filled with evaporated sample of 30 mL and submerged in a water bath maintained at each measurement temperature. The cylinder was shaken in the water bath for 8 min until the temperature of the sample inside the cylinder was constant, and pressure rise in the cylinder was measured as a vapor pressure.

2.3. Flash point measurement

Flashpoints were measured by an automated closed cup flash point tester (Tanaka Scientific Ltd. AVP-30D). The closed-cup flash point tests were carried out in accordance with JIS K 2265-1. A degraded fuel mixture of 50 mL was put into a sample cup, and the cup was covered with a lid. A pilot flame was brought close to

the inner space of the cup from an observation hatch at the intervals of 0.5 °C, while heating the sample at a rising rate of 1 °C/min. The flash point was defined as the lowest temperature where a flash was observed. The procedures after covering the cup were automated. Each sample was examined three times, and the lowest temperature was considered to be the flash point. Flash points of less than –30 °C cannot be measured, because a refrigerator cannot cool liquid refrigerant to less than –40 °C.

2.4. Evaporation rate measurement

Evaporation rates were measured by weight loss using an electronic balance. The balance was a Sartorius CP4202S, capable of measurements to 0.01 g. A tarred square pan (base area: 0.1 m^2) was loaded on the balance, and a fuel mixture was poured into the pan, then the weight loss was measured with time. The data was recorded by PC at time intervals of 10 s until the weight loss fraction reached 0.3. The experiments were conducted in a fume hood. The fume hood fan was not operated, and the fuel mixture was evaporated in a no wind condition. The amount of the poured fuel mixture was 200 mL (thickness of the fuel d : 2 mm). A K-type thermocouple of 80 μm diameter was put on the base of the pan, and the temperature of the fuel mixture was measured.

2.5. Evaporation and diffusion experiment

Evaporation and diffusion experiments were carried out using a cylindrical vessel of 60 cm diameter and 100 cm height with an opening on the top. A 1:1 fuel mixture (thickness of fuel spill d : 1, 2 and 3 mm) was gently spilt over the whole surface of the vessel base. Concentrations of fuel vapor were measured on various time t at the designated height h ($h=10, 20, 30, 40$ and 50 cm). Every experiment was carried out at 19 °C. The experimental apparatus of evaporation and diffusion from a fuel spill is shown in Fig. 1. The concentrations of fuel vapor were measured by infrared

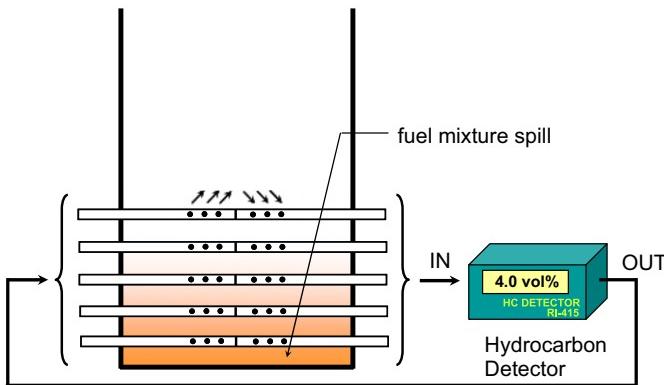


Fig. 1. Experimental apparatus of evaporation and diffusion from gasoline spill on a floor.

hydro carbon detectors (Riken Keiki Co. Ltd. RI-415), which were calibrated using standard *iso*-butane. These experiments were carried out in a sufficiently large room, and we can consider the concentration of fuel vapor outside the vessel to be zero.

2.6. Ignition experiment of fuel vapor

Ignition experiments were carried out using a cubic steel frame vessel of 1 m³ with a base plate in order to verify the concentration distribution of fuel vapor predicted by the evaporation and diffusion model. The frame was covered with a vinyl sheet. A 1:1 fuel mixture of 1 L (thickness of fuel spill d : 1 mm) was gently poured into the vessel using vinyl hose and spilt over the whole surface of the vessel base. Then, a spark discharge was generated in the vessel using a 6000 V neon sign transformer (the gap of electrode was 2 mm), and observed the existence of ignition to the fuel vapor evaporated from the fuel spill. Sparks were generated at various ignition heights h_i in a fixed time t_i ($t_i=5, 10, 20$ and 30 min) after the spill. The heights where sparks were generated were designed at 10, 20, 30 and 40 cm. The experimental apparatus is shown in Fig. 2.

3. Results and discussion

3.1. Vapor pressure of fuel mixtures

The relation between vapor pressure p [Pa] and temperature T [K] in a multi-component fuel mixture can be explained by the following Clausius–Clapeyron equation [8,9].

$$\ln p = A - B/T \quad (2)$$

where A, B are the Clausius–Clapeyron constants [-] and A is equivalent to the quotient of the evaporation enthalpy by the gas constant. While the Clausius–Clapeyron equation is well established for pure substances, it is reported that the equation is applied for gasoline and the constants of gasoline are linearly related to the weight loss fraction a [10].

$$A = \alpha_A a + \beta_A \quad (3)$$

$$B = \alpha_B a + \beta_B \quad (4)$$

Substituting Eqs. (3) and (4) into the Clausius–Clapeyron equation yields

$$\ln p = (\alpha_A - \alpha_B/T)a + (\beta_A - \beta_B/T)a \quad (5)$$

$$p = \exp(\beta_A - \beta_B/T) \exp\{(\alpha_A - \alpha_B/T)a\} \quad (6)$$

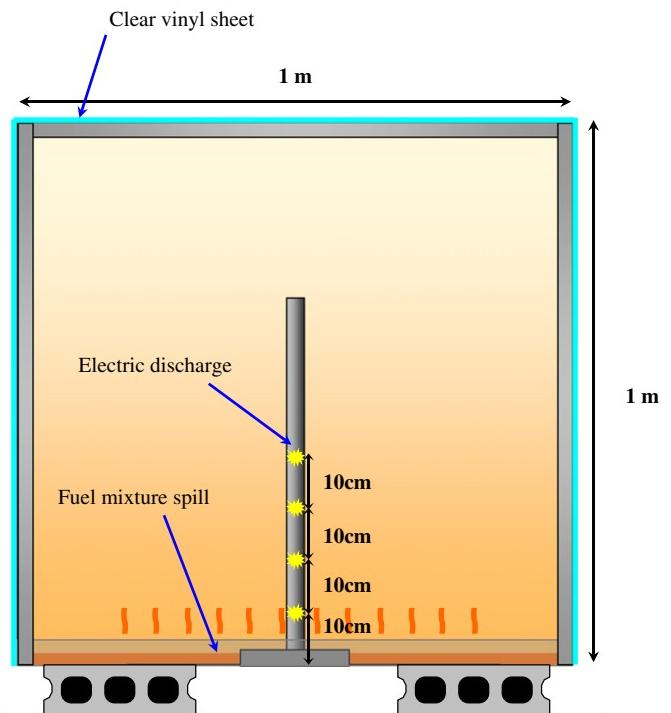


Fig. 2. Experimental apparatus to ignite the fuel vapor above the mixed fuel spill on a floor.

Table 1
Evaporation constants used in the prediction model.

Fuel	α_A (-)	β_A (-)	α_B (-)	β_B (-)	k (m/s)
Gasoline	1.49	21.0	1.74×10^3	3.03×10^3	3.15×10^{-4}
Kerosene	46.4	28.7	1.69×10^4	7.06×10^3	2.25×10^{-4}

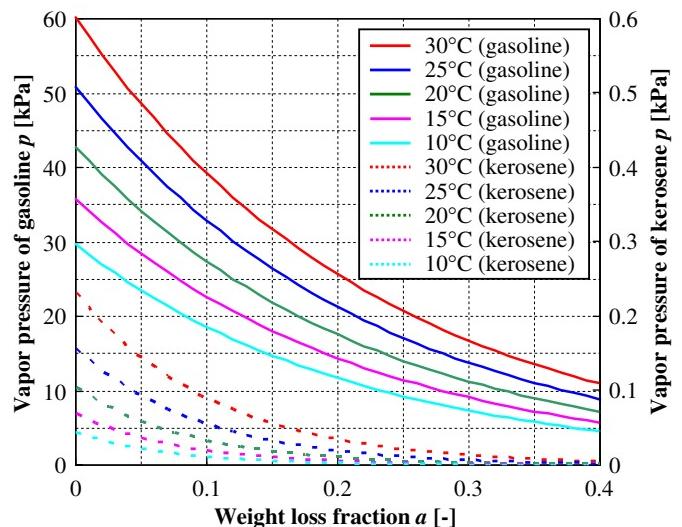


Fig. 3. Variation of vapor pressure of gasoline and kerosene with progress of evaporation.

Thus, if the temperature is constant, the change in the vapor pressure by evaporation can be expressed by an exponential function of the weight loss fraction. Since kerosene is a multi-component hydrocarbon mixture as well as gasoline, it was assumed that Clausius–Clapeyron equation was established in kerosene. The values of α_A , β_A , α_B and β_B were obtained from the

measured vapor pressure of degraded samples of gasoline and kerosene, respectively. These values are called “vapor pressure constant” and shown in Table 1. The change in vapor pressure of gasoline can be obtained from the constants using Eq. (6), and change curves in the vapor pressure by evaporation are shown in Fig. 3. After the following section, the vapor pressures of degraded fuel mixtures were predicted using the constants presented in Table 1.

The evaporation model of a multi-component liquid was presented in the previous work [11]. While gasoline and kerosene are multi-component fuel, we expressed the vapor pressure of each fuel by an exponential function of a weight loss fraction and assumed that the fuel mixtures are two-component liquids of gasoline and kerosene. Then, the variation of the composition of a fuel mixture by evaporation was predicted.

The composition of the released vapor from a fuel surface was assumed to be equal to that of the gas phase that was in equilibrium with the liquid phase. In other words, the molar fraction of each component in vapor, y_g and y_k was expressed as

the proportion of each partial vapor pressure to the total vapor pressure as shown in Eqs. (7) and (8).

$$y_g = x_g p_g / (x_g p_g + x_k p_k) \quad (7)$$

$$y_k = x_k p_k / (x_g p_g + x_k p_k) \quad (8)$$

where x_g and x_k are the molar fraction of gasoline and kerosene component in liquid fuel, and p_g and p_k are the vapor pressure of gasoline and kerosene component in the pure state.

When a small amount of a fuel mixture, dw [kg] was vaporized, molar amount in the vapor mixture of each component dN_i [mol] was respectively calculated as shown in Eqs. (9) and (10).

$$dN_g = y_g dw / (y_g M_g + y_k M_k) \quad (9)$$

$$dN_k = y_k dw / (y_g M_g + y_k M_k) \quad (10)$$

where M_g is the molecular weight of gasoline (0.08 kg/mol) and M_k is that of kerosene (0.12 kg/mol). Since gasoline and kerosene are multi-component fuel, the average molecular weights increase with

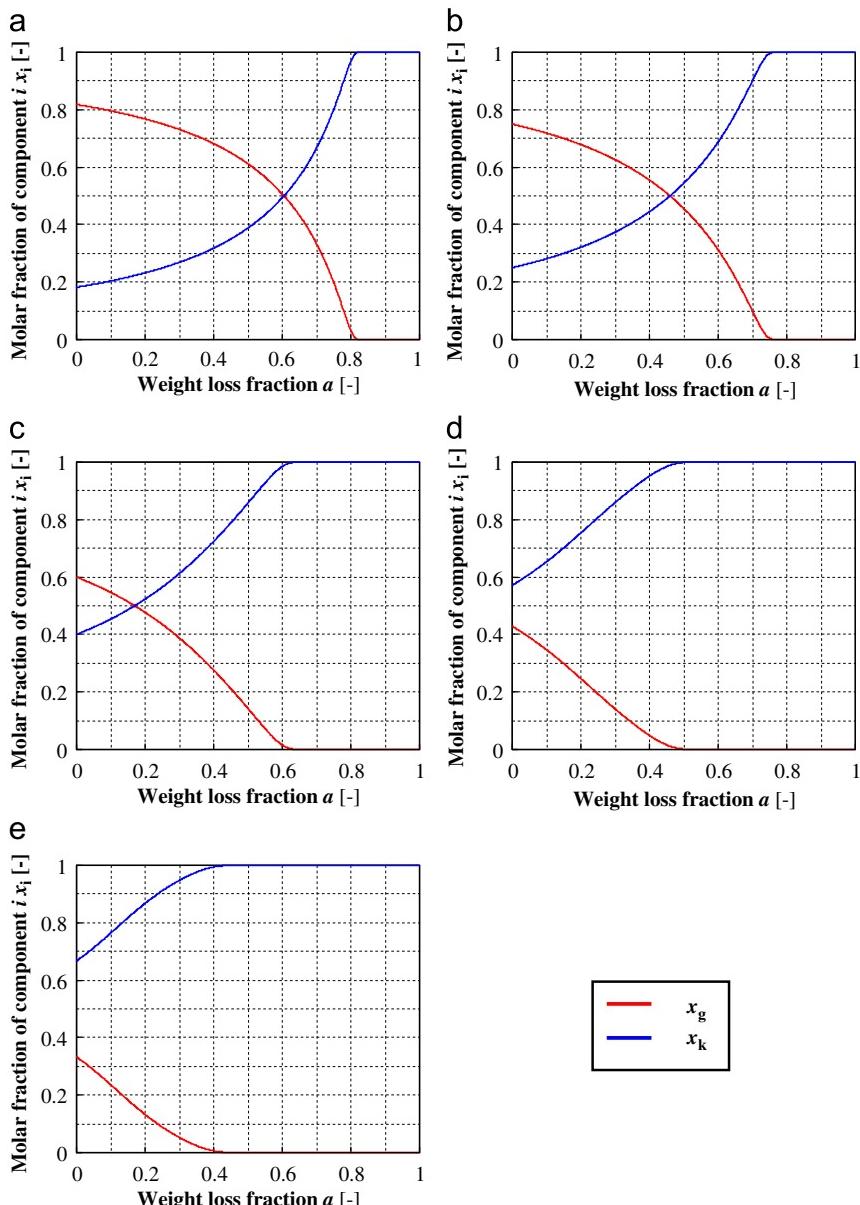


Fig. 4. Variation of molar fraction of each component in liquid phase with progress of evaporation at 20 °C. (a) 3:1 fuel mixture. (b) 2:1 fuel mixture. (c) 1:1 fuel mixture. (d) 1:2 fuel mixture. (e) 1:3 fuel mixture.

the progress of evaporation. In this work, the molecular weights were assumed to be constant (0.08 and 0.12 kg/mol, respectively) in order to present a simple evaporation model.

As mentioned in Section 3.1, the vapor pressure of gasoline and kerosene, p_g and p_k were given by

$$p_g = \exp(\beta_{A,g} - \beta_{B,g}/T) \exp\{(\alpha_{A,g} - \alpha_{B,g}/T)a_g\} \quad (11)$$

$$p_k = \exp(\beta_{A,k} - \beta_{B,k}/T) \exp\{(\alpha_{A,k} - \alpha_{B,k}/T)a_k\} \quad (12)$$

where a_g and a_k are the weight loss fraction of gasoline and kerosene, respectively.

The variation of the molar fraction of gasoline and kerosene compartment in fuel mixtures with the progress of evaporation was calculated by using Eqs. (7)–(12). The variations of the molar fraction in 3:1, 2:1, 1:1, 1:2 and 1:3 fuel mixtures at 20 °C by

evaporation are shown in Fig. 4. The variations of the weight loss fraction of gasoline and kerosene are shown in Fig. 5. The results showed that the gasoline component were preferentially lost in every fuel mixture.

If fuel mixture was assumed to be ideal liquid, then vapor pressure of fuel mixture was calculated by Eq. (13).

$$\begin{aligned} p &= x_g p_g + x_k p_k \\ &= x_g \exp(\beta_{A,g} - \beta_{B,g}/T) \exp\{(\alpha_{A,g} - \alpha_{B,g}/T)a_g\} \\ &\quad + x_k \exp(\beta_{A,k} - \beta_{B,k}/T) \exp\{(\alpha_{A,k} - \alpha_{B,k}/T)a_k\} \end{aligned} \quad (13)$$

The vapor pressure of the fuel mixture in the various weight mixture ratios at 10–25 °C was calculated by using Eq. (13). The calculated and measured vapor pressures are shown in Fig. 6. In every fuel mixture, the calculated vapor pressure agreed well with the measured one. It was found that the change in the vapor

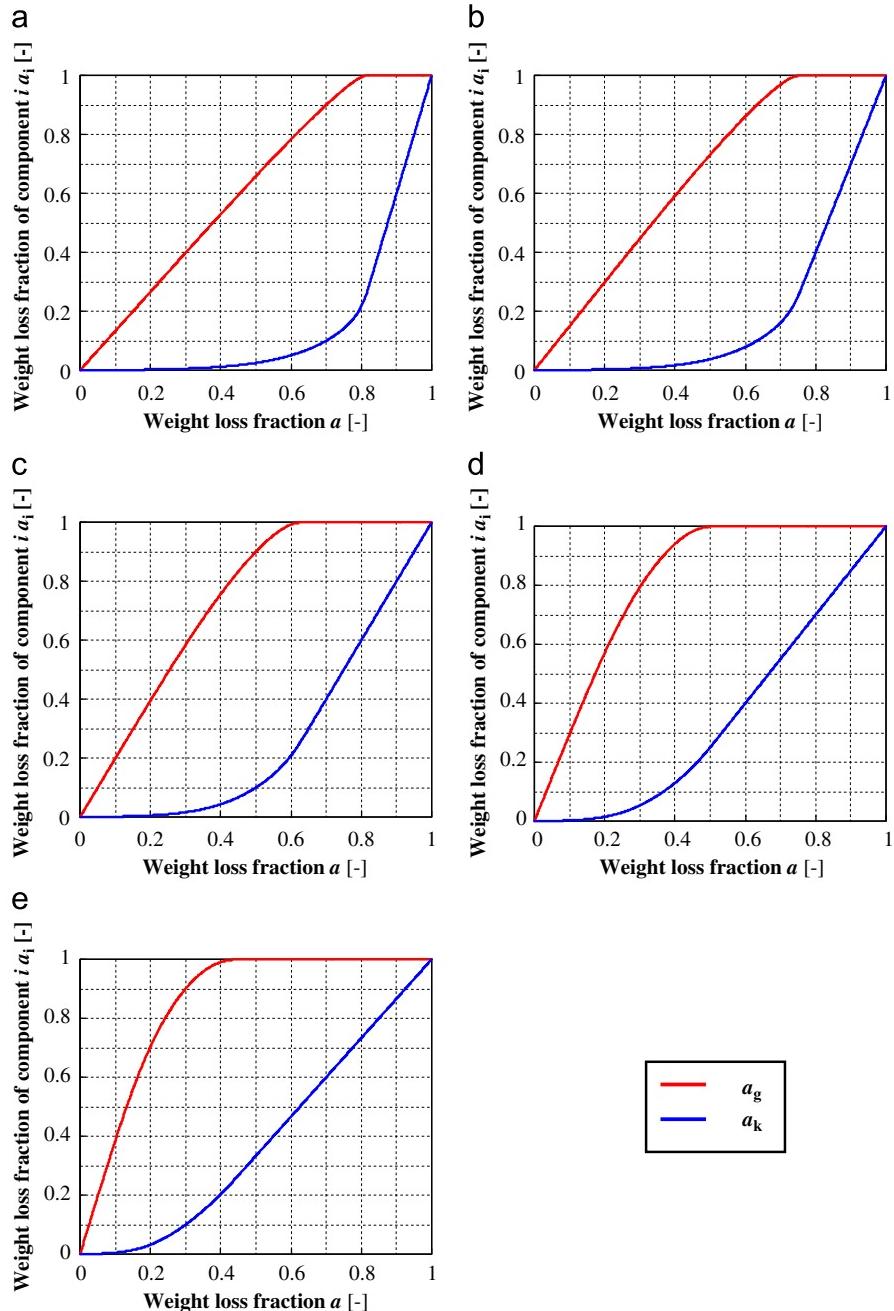


Fig. 5. Variation of weight loss fraction of each component in liquid phase with progress of evaporation at 20 °C. (a) 3:1 fuel mixture. (b) 2:1 fuel mixture. (c) 1:1 fuel mixture. (d) 1:2 fuel mixture. (e) 1:3 fuel mixture.

pressure with the progress of evaporation of fuel mixture could be predicted accurately by using the evaporation model.

Then, the changes in the vapor pressures of 3:1, 2:1, 1:1, 1:2 and 1:3 fuel mixtures at 10–40 °C by evaporation were calculated. The obtained vapor pressures of fuel mixtures were plotted by Clausius–Clapeyron equation as shown in Fig. 7. They were shown to lie almost on a straight line; therefore, the vapor pressure constants of the fuel mixtures were obtained from the intercepts and slopes of the plots and were shown in Table 2. The vapor pressure of the degraded fuel mixture at an arbitrary temperature can be calculated using these vapor pressure constants and Eq. (6).

If the vapor pressure constant of gasoline and kerosene are obtained, vapor pressure of fuel mixture in an arbitrary mixture ratio can be accurately predicted in the method described above.

3.2. Flash point of fuel mixtures

At the flash point, the concentration of vapor on a fuel surface is equal to the lower explosive limit (LEL) of the fuel vapor–air mixture. Since vapor generated from fuel mixtures is almost composed of gasoline component as shown in Fig. 5, the LEL of a fuel vapor–air mixture was assumed to be similar to that of a gasoline–air mixture, 1.4 vol% [12]. The predicted flash points of degraded samples of fuel mixtures were obtained by calculating the temperature, where the concentration of vapor on a fuel surface is equal to the LEL, i.e., the vapor pressure is equivalent to 1420 Pa, using Eq. (6) that expresses the relation between temperature and vapor pressure. The flash point T_f is given by

$$T_f = \frac{\alpha_B a + \beta_B}{\alpha_A a + \beta_A - \ln(1420)} \quad (14)$$

The change in the flash points of three kinds of fuel mixtures (2:1, 1:1 and 1:2 fuel mixture) by evaporation were calculated by using Eq. (14) and the vapor pressure constants presented in Table 2. The measured and predicted flash points are shown in Fig. 8. The predicted flash points almost agreed with the measured results. In the degraded 2:1 fuel mixtures of $a \leq 0.1$, the degraded 1:1 fuel mixtures of $a \leq 0.05$ and the 1:2 fuel mixture, the flash points could not be measured because they are –30 °C or less. The flash point of the fuel mixtures rose as evaporation progressed, and the flash point of the degraded 1:2 fuel mixture of $a=0.25$ especially rose up to around 40 °C.

The vapor pressure of fuel mixture in an arbitrary mixture ratio was expressed by Eq. (13). Substituting 0 for a in Eq. (13) and replacing molar fraction of gasoline x_g with initial weight fraction X_{g0} , the relation between the flash point of non-degraded fuel mixture T_f and initial weight fraction X_{g0} , is given by

$$1.4 = \frac{M_k X_{g0}}{M_k X_{g0} + M_g (1-X_{g0})} \exp(\beta_{A,g} - \beta_{B,g}/T_f) + \frac{M_g (1-X_{g0})}{M_k X_{g0} + M_g (1-X_{g0})} \exp(\beta_{A,k} - \beta_{B,k}/T_f) \quad (15)$$

The change of the flash point by mixing gasoline into kerosene was calculated by using Eq. (15). It was found that the flash point of kerosene rapidly decreased by the contamination of gasoline as shown in Fig. 9.

3.3. Evaporation rates of fuel mixtures

The evaporation rate of a multi-component liquid is in proportion to the vapor pressure p [Pa] as follows [13]:

$$\nu = kpM/RT \quad (16)$$

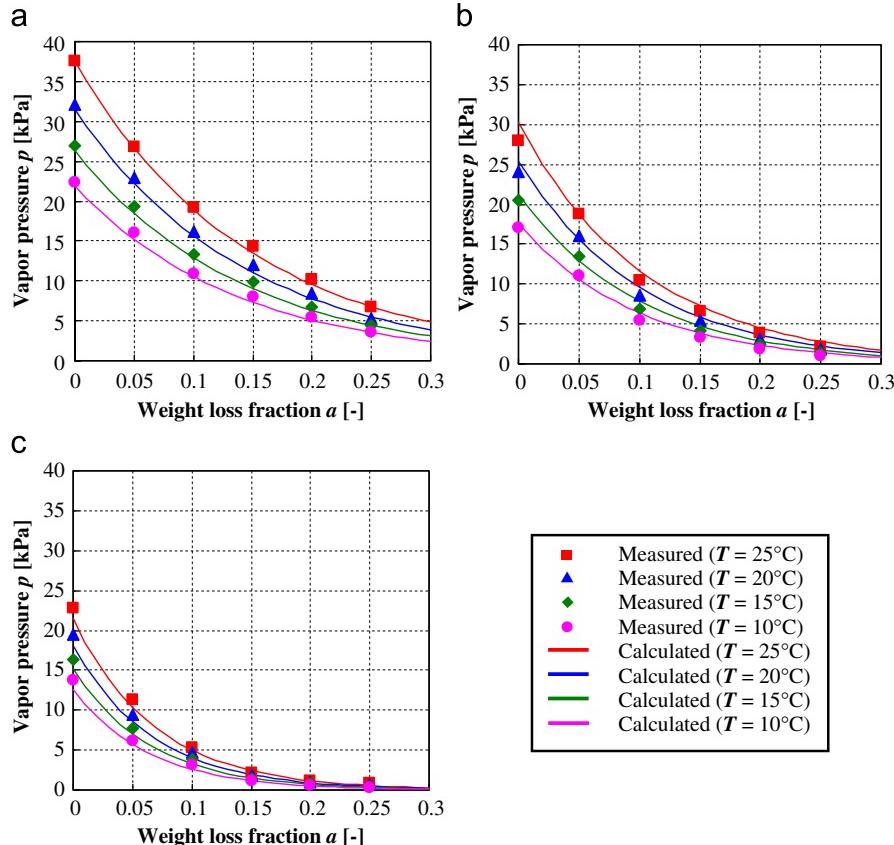


Fig. 6. Measured and calculated vapor pressure of mixed fuel. (a) 2:1 fuel mixture. (b) 1:1 fuel mixture. (c) 1:2 fuel mixture.

where k is the mass transfer coefficient [m/s], M is the molecular weight [kg/mol], R is the gas constant (8.314 J/mol K) and T is the temperature [K]. The molecular weight of gasoline and kerosene were assumed constant at 0.08, 0.12 kg/mol, respectively. The mass transfer coefficients of gasoline and kerosene were, respectively, obtained from the slope of the approximate straight lines by plotting the evaporation rate against the value of pM/RT . The mass transfer coefficients were shown in Table 1.

Correlations of weight loss fractions with evaporation rates of fuel mixtures were shown in Fig. 10. The evaporation rates of fuel mixtures decreased gradually with the progress of evaporation because more volatile components were lost by evaporation. The evaporation rate of a multi-component liquid mixture can be expressed by the sum of the products of evaporation rate and molar fraction in each component [14]. The fuel mixtures of gasoline and kerosene were assumed to be two-component liquids, so the evaporation rate was given by

$$\nu = x_g \nu_g + x_k \nu_k = x_g k_g p_g M_g / RT + x_k k_k p_k M_k / RT \quad (17)$$

where k_g, k_k are the mass transfer coefficients of each component [m/s]. The coefficients were, respectively, obtained from the

measured evaporation rates of gasoline and kerosene as shown in Table 1.

The changes in the evaporation rates of 3:1, 2:1, 1:1, 1:2 and 1:3 fuel mixtures by evaporation were calculated by using Eq. (17), and they were compared with the measured one as shown in Fig. 10. In every fuel mixture, the calculated evaporation rate agreed well with the measured one. The change in evaporation rates with the progress of evaporation of fuel mixtures could be predicted accurately, assuming the fuel mixtures of gasoline and kerosene were the two-component liquids.

3.4. Amount of the generated vapor from a fuel mixture spill

The changes in the evaporation rates of 3:1, 2:1, 1:1, 1:2 and 1:3 fuel mixtures at 10–25 °C by evaporation were calculated by using Eq. (17), and presented in Fig. 11. The logarithm of the obtained evaporation rates are plotted against the weight loss fractions in Fig. 12. The plots indicate linear relationships. Therefore, the relation between a weight loss fraction and an evaporation rate can be approximately expressed by an exponential

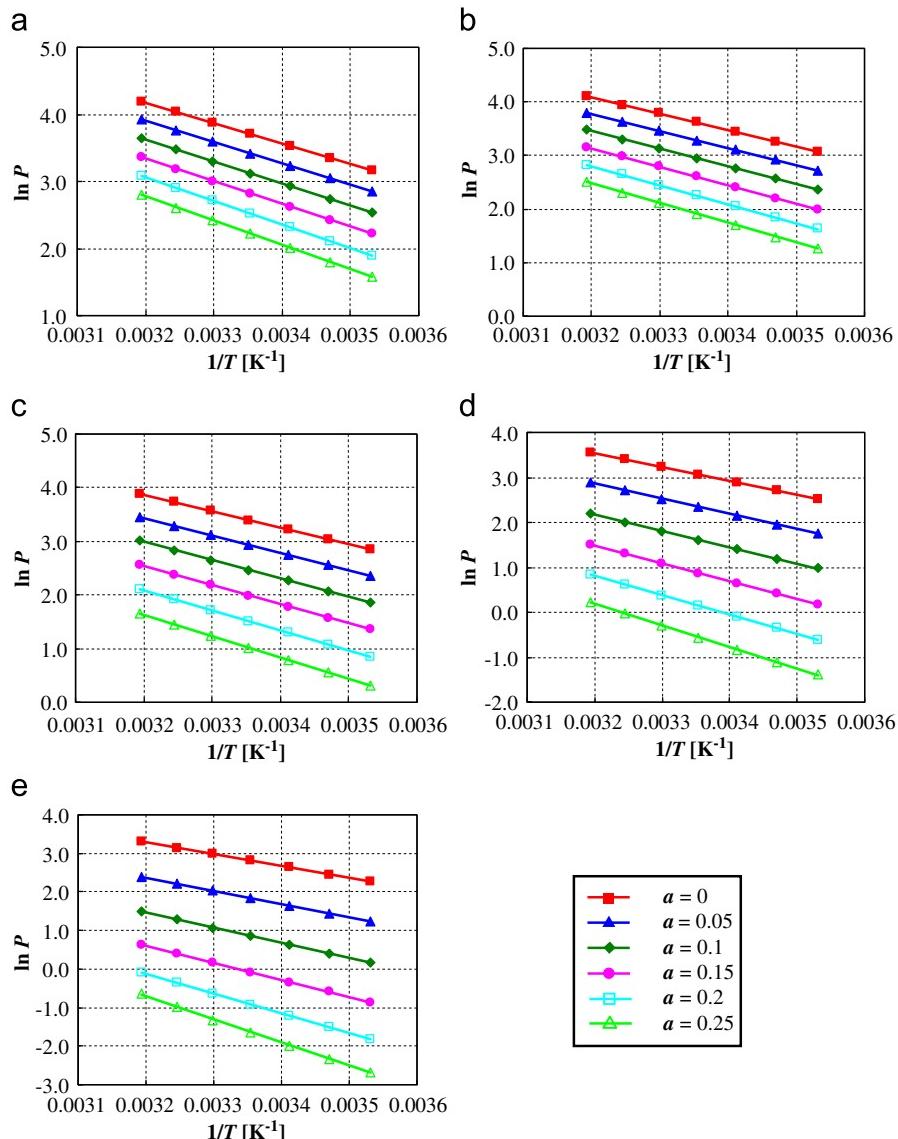


Fig. 7. Clausius-Clapeyron plots of fuel mixtures. (a) 3:1 fuel mixture. (b) 2:1 fuel mixture. (c) 1:1 fuel mixture. (d) 1:2 fuel mixture. (e) 1:3 fuel mixture.

function.

$$v = me^{-na} \quad (18)$$

where m and n are the evaporation rate constants. These constants were respectively obtained from the intercepts and slopes of the approximate straight lines as shown in Table 3.

The evaporation rate v [$\text{kg}/\text{m}^2 \text{s}$] is the weight loss per dt and unit area and is expressed as:

$$v = -(1/S) \cdot (dw/dt) \quad (19)$$

where w is the current weight of a fuel mixture [kg], S is the evaporative area [m^2] and t is time [s]. Eq. (19) is replaced by Eq. (18):

$$-(1/S) \cdot (dw/dt) = m \exp(-na) \quad (20)$$

where

$$dw = -w_0 da \quad (21)$$

Eq. (20) is rewritten to:

$$\exp(na) da = \frac{mS}{w_0} dt \quad (22)$$

The boundary condition for Eq. (22) is:

$$a = 0 \text{ at } t = 0 \quad (23)$$

Table 2
Vapor pressure constants of fuel mixtures.

Fuel	α_A	β_A	α_B	β_B
3:1 fuel mixture	1.80	20.8	2.36×10^3	3.03×10^3
2:1 fuel mixture	2.00	20.7	2.69×10^3	3.03×10^3
1:1 fuel mixture	2.95	20.5	3.79×10^3	3.03×10^3
1:2 fuel mixture	8.76	20.0	7.04×10^3	2.97×10^3
1:3 fuel mixture	21.2	19.2	1.18×10^4	2.86×10^3

Eq. (22) can be solved as:

$$a = \frac{1}{n} \ln \{ mnSt/w_0 + 1 \} \quad (24)$$

Multiplying the both sides of Eq. (24) by w_0 , the amount of evaporated fuel mixture aw_0 is given by:

$$aw_0 = \frac{w_0}{n} \ln \{ mnSt/w_0 + 1 \} \quad (25)$$

Thus, the amount of evaporated fuel mixture is expressed by logarithm of time. The amount of evaporated fuel mixture after an arbitrary time passes can be estimated using Eq. (25).

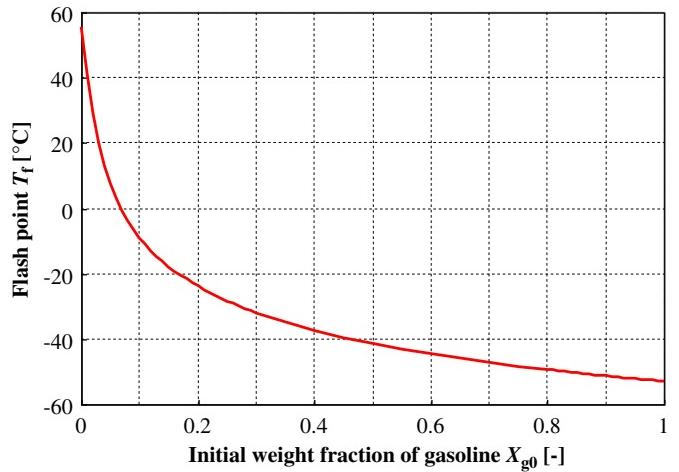


Fig. 9. Variation of flash point of fuel mixture with varying initial weight fraction of gasoline.

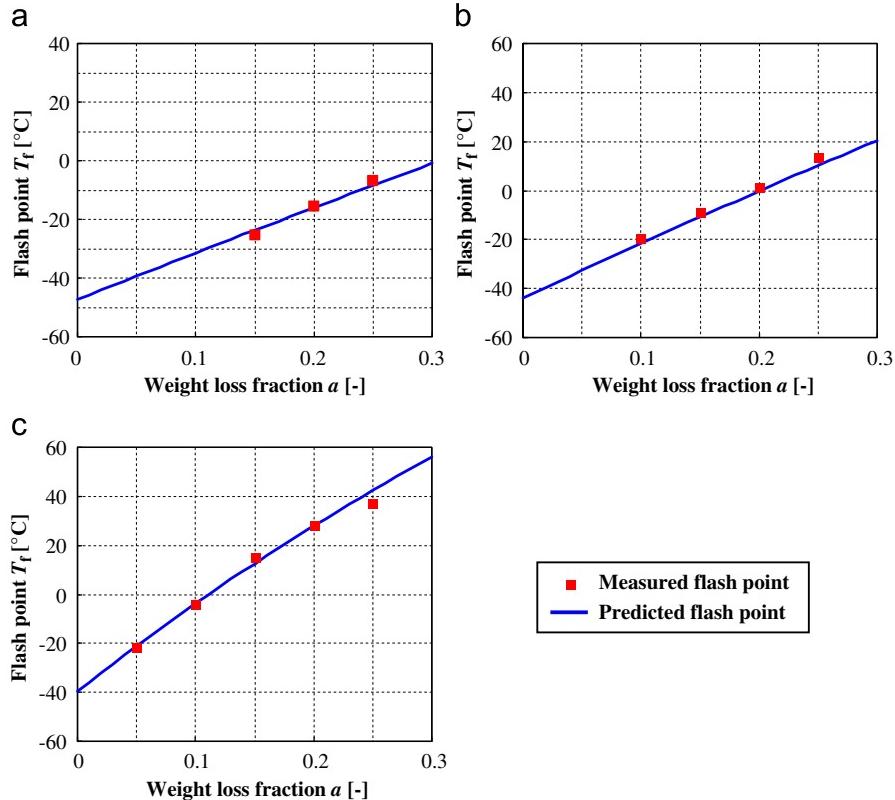


Fig. 8. Measured and predicted flash points of degraded gasoline. (a) 2:1 fuel mixture. (b) 1:1 fuel mixture. (c) 1:2 fuel mixture.

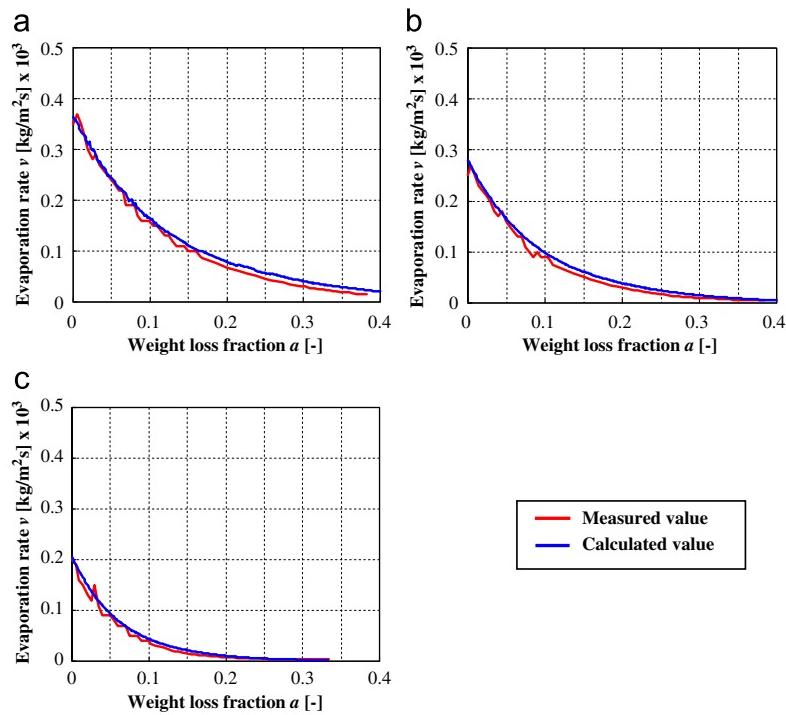


Fig. 10. Measured and calculated evaporation rate from a fuel spill of 2 mm thickness. (a) 2:1 fuel mixture. (b) 1:1 fuel mixture. (c) 1:2 fuel mixture.

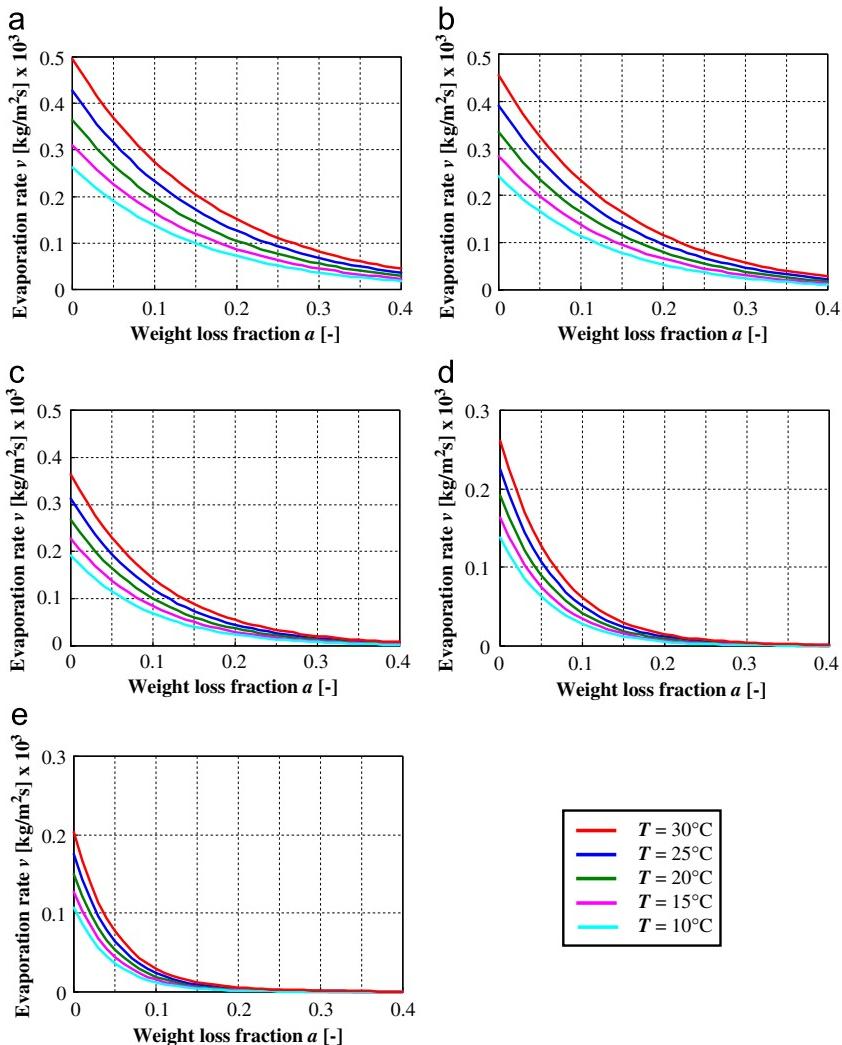


Fig. 11. Evaporation rate curves with varying temperature. (a) 3:1 fuel mixture. (b) 2:1 fuel mixture. (c) 1:1 fuel mixture. (d) 1:2 fuel mixture. (e) 1:3 fuel mixture.

Replacing St/w_0 by a standardized time θ [m^2/s], Eq. (25) is rewritten by

$$a = \frac{1}{n} \ln \{mn\theta + 1\} \quad (26)$$

By illustrating the relation between a standardized time θ and a , an evaporation characteristics curve, which is independent of the evaporative condition such as the spill area and the amount of spilt fuel (i.e., the thickness of spilt fuel), can be obtained. The evaporation characteristics curves of 3:1, 2:1, 1:1, 1:2 and 1:3 fuel mixtures at 10–30 °C are shown in Fig. 13 using m and n presented in Table 3. The amount of the evaporated fuel mixture in an arbitrary evaporative condition can be read off from the curve by calculating the corresponding θ value. Thus, if the mixture ratio of a fuel mixture is known, the amount of the generated vapor in an arbitrary spill condition can be estimate by the method described above.

3.5. Evaporation and diffusion experiment

The concentration distribution of the vapor generated from a gasoline spill on a floor can be predicted by the unidimensional diffusion model [7]. The vapor pressures of fuel mixtures decrease

with the progress of evaporation. Therefore, the concentration on the surface of a fuel mixture needs to be changed correspondingly with the progress of evaporation. The concentration of vapor on the surface of a fuel mixture was expressed by the ratio of the vapor pressure to the atmospheric pressure, and is given by

$$C_{0,t} = \frac{p}{p_0} = \frac{\exp(\beta_A - \beta_B/T) \exp\{(\alpha_A - \alpha_B/T)a\}}{p_0} \quad (27)$$

where p_0 is the atmospheric pressure (101,300 Pa), a is the weight loss fraction, which is obtained from the accumulated amount of the evaporated fuel mixture, T is the temperature of a fuel mixture [K] and $\alpha_A, \alpha_B, \beta_A$ and β_B are the vapor pressure constants of fuel mixtures, the constants presented in Table 2.

Let us consider the unidimensional vertical diffusion in the z -direction through an infinite plane space, of thickness Δz [m] (Fig. 14). The upward volumetric flux at time t and height z , $J_{z,t}$ [$\text{m}^3/\text{m}^2\text{s}$] ($= m/\text{s}$) is given by

$$J_{z,t} = D(C_{z,t} - C_{z+\Delta z,t})/\Delta z \quad (28)$$

where D is the diffusion constant [m^2/s], $C_{z,t}$ is the concentration of vapor at time t and height z .

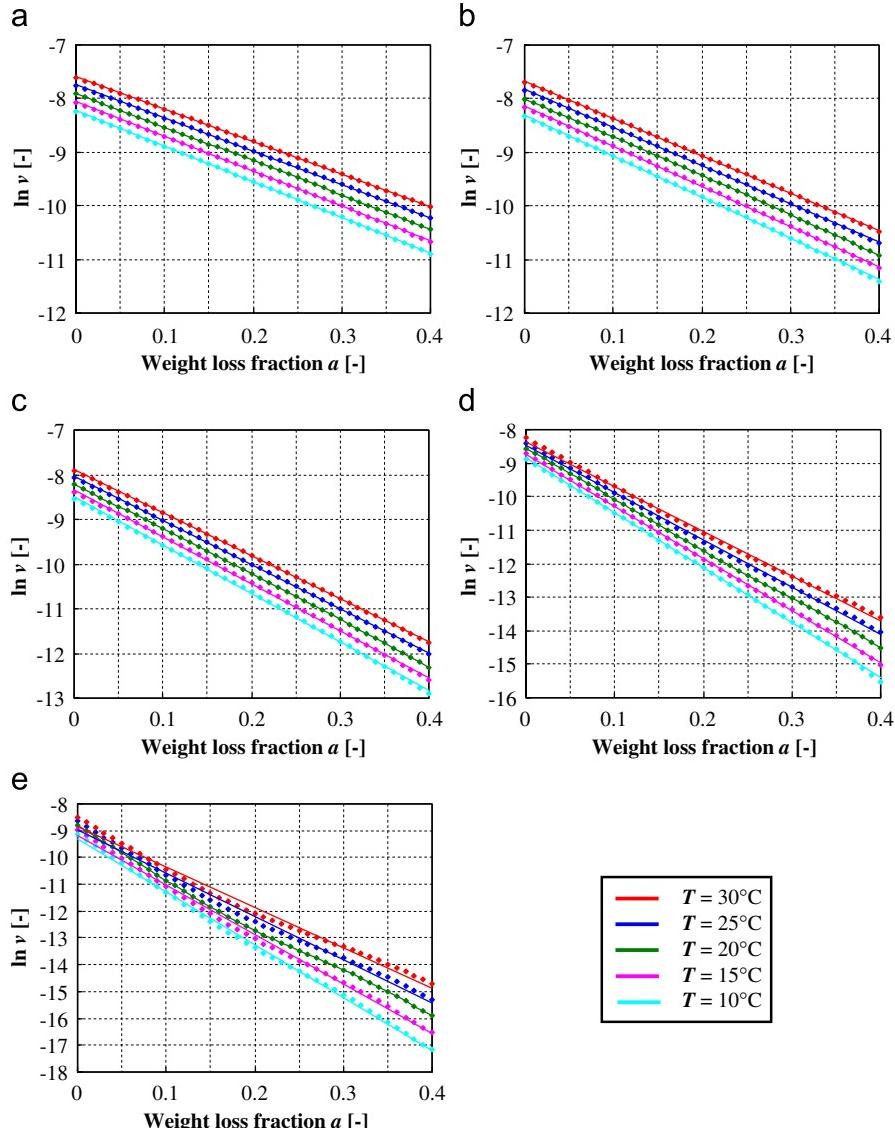


Fig. 12. $a=\ln v$ plots of mixed fuel. (a) 3:1 fuel mixture. (b) 2:1 fuel mixture. (c) 1:1 fuel mixture. (d) 1:2 fuel mixture. (e) 1:3 fuel mixture.

Taking the mass balance in the space at time t and height z , the concentration changes of vapor $\Delta C_{z,t}$ in a very short time Δt is expressed as:

$$\Delta C_{z,t} = (J_{z-\Delta z,t} - J_{z,t})\Delta t/\Delta z \quad (29)$$

where $J_{z-\Delta z,t}$ is the influx at height $z-\Delta z$, $J_{z,t}$ is the outflux at height z .

Substituting Eq. (28) into Eq. (29) gives

$$\Delta C_{z,t} = D(C_{z-\Delta z,t} - 2C_{z,t} + C_{z+\Delta z,t})\Delta t/\Delta z^2 \quad (30)$$

Table 3

Evaporation rate constants of fuel mixtures.

Temperature T (°C)	Fuel									
	3:1 fuel mixture		2:1 fuel mixture		1:1 fuel mixture		1:2 fuel mixture		1:3 fuel mixture	
	m [-]	n [-]								
30	5.02×10^{-4}	6.04	4.63×10^{-4}	6.95	3.73×10^{-4}	9.59	2.35×10^{-4}	13.4	1.43×10^{-4}	15.1
25	4.32×10^{-4}	6.18	3.99×10^{-4}	7.12	3.23×10^{-4}	9.89	2.08×10^{-4}	14.1	1.28×10^{-4}	16.1
20	3.69×10^{-4}	6.32	3.41×10^{-4}	7.29	2.78×10^{-4}	10.2	1.84×10^{-4}	14.8	1.15×10^{-4}	17.3
15	3.14×10^{-4}	6.47	2.91×10^{-4}	7.47	2.38×10^{-4}	10.5	1.62×10^{-4}	15.6	1.03×10^{-4}	18.5
10	2.66×10^{-4}	6.62	2.46×10^{-4}	7.64	2.03×10^{-4}	10.8	1.42×10^{-4}	16.4	9.17×10^{-5}	19.7

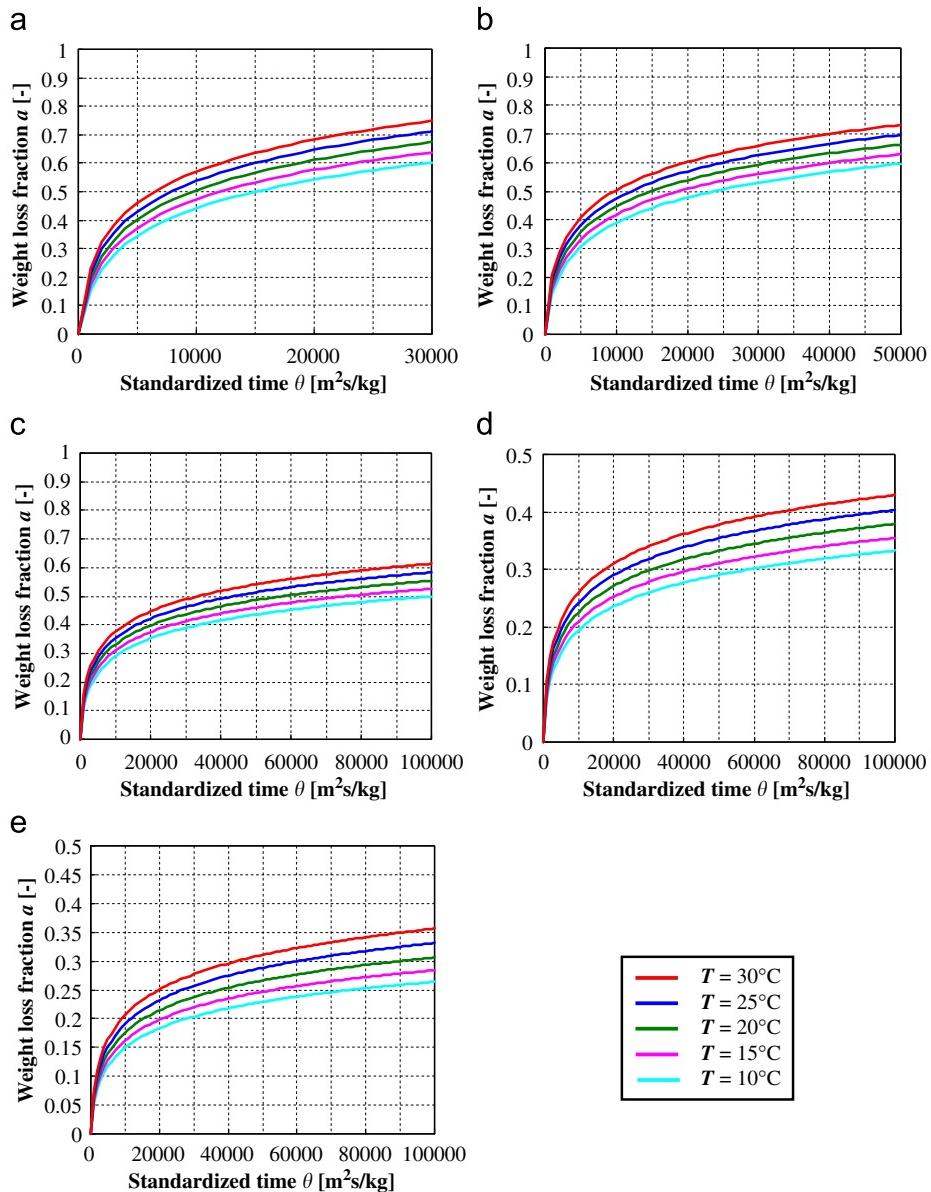


Fig. 13. Evaporation characteristics curves. (a) 3:1 fuel mixture. (b) 2:1 fuel mixture. (c) 1:1 fuel mixture. (d) 1:2 fuel mixture. (e) 1:3 fuel mixture.

The concentration distributions of fuel vapor were calculated by numerically integrating Eq. (30) with an initial condition $C_0=0$ at $t=0$, in increasing Δt of 1 s and Δz of 0.5 cm. The vapor concentration on the fuel surface, which was the boundary condition, was calculated by Eq. (27) using the ambient temperature. Since vapor generated from fuel mixtures was almost composed of gasoline component as shown in Fig. 5, the physical properties of fuel mixtures can be expected to be similar to that of gasoline. The diffusion constant of fuel vapor D was assumed to be $1.0 \times 10^{-5} \text{ m}^2/\text{s}$ as well as that of gasoline vapor [7]. The calculated concentrations at every 10 cm height from the base up to 50 cm height in the cylindrical vessel for an hour after the spill of a 1:1 fuel mixture are compared with the measured results as shown in Fig. 15. The concentration of the vapor increased at each height over time. The increases were greater in the case of the fuel depth at 2 mm than 1 mm. The reason is that the amount of low-boiling point component is more, and the chemical component composition changes more slowly at 2 mm than at 1 mm. The calculated vapor concentrations agreed well with the measured results. It was found that the concentration of the vapor generated from a fuel

mixture spill on a floor can be predicted by using the presented diffusion model.

The concentrations of vapor generated from fuel mixture spills in various mixture ratios were predicted using the vapor pressure constants presented in Table 2. The time variations of the concentrations in every height are shown in Fig. 16. In the higher weight fraction of gasoline, the vapor concentration was estimated to become higher. Thus, evaporation and diffusion behavior of fuel mixtures of gasoline and kerosene in an arbitrary mixture ratio can be predicted by the evaporation model of the fuel mixture and the unidimensional diffusion model.

3.6. Ignition experiment of fuel vapor

Ignition experiments were carried out in order to verify the predicted concentration distribution of fuel vapor in the evaporation and diffusion experiments. "Ignition" or "non-ignition" to the vapor above the fuel mixture spills on the base of the frame vessel was observed when a spark discharge was generated in various elapsed times at various heights. The experiments were carried out at 23–24 °C. The combustion behavior in the experiment where the flammable mixture was ignited at 20 cm height in 30 min after the fuel spill were shown in Fig. 17. The flame spherically propagated in the flammable mixture and soon reached the upper and lower end of the flammable mixture. Subsequently, the flame was no longer advanced and propagated only horizontally as shown in Fig. 17. From the results, it was confirmed that the layer concentration distribution with a negative gradient was formed above a fuel mixture spill.

The vapor concentrations in the frame vessel were calculated by the above-mentioned evaporation and diffusion model of fuel mixture. Since the component of vapor generated from a fuel mixture of gasoline and kerosene can be expected to be similar to that of gasoline vapor, the flammable range of the fuel vapor-air

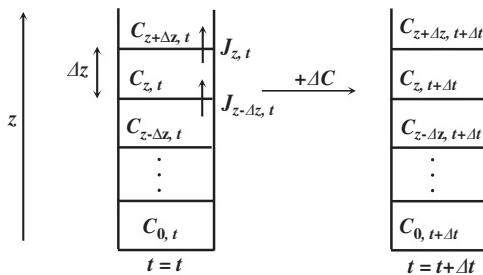


Fig. 14. Vertical diffusion model of fuel vapor.

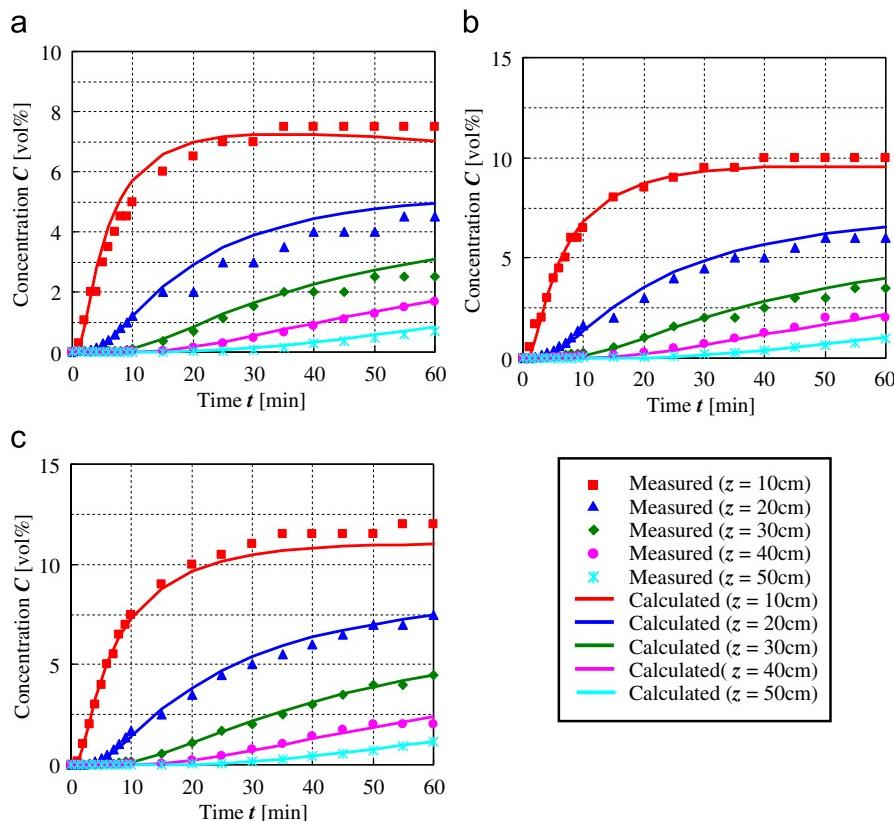


Fig. 15. Measured and predicted concentration of vapor when 1:1 fuel mixture was spilt on a floor. (a) $d=1\text{ mm}$. (b) $d=2\text{ mm}$. (c) $d=3\text{ mm}$.

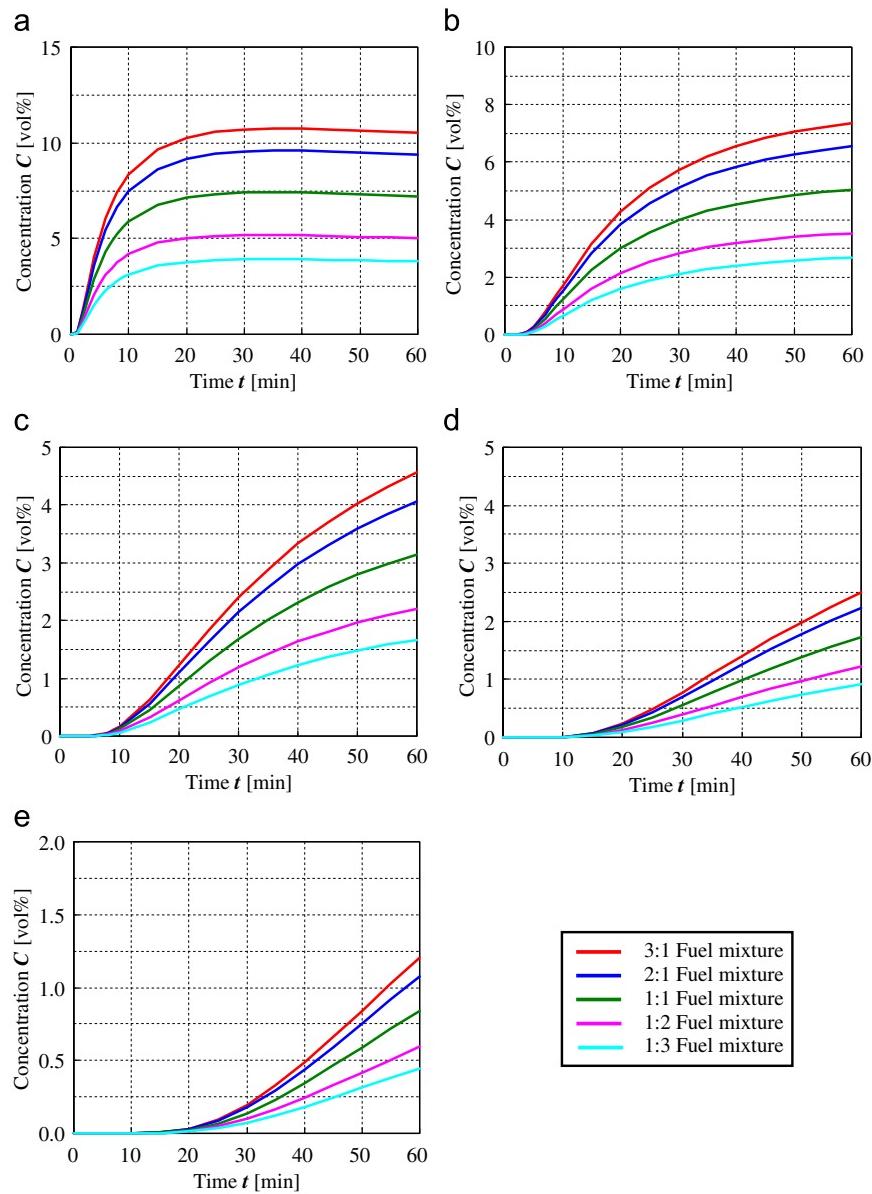


Fig. 16. Predicted concentration of vapor when fuel mixture was spilled on floor with 1 mm thickness at 20 °C. (a) $z=10$ cm. (b) $z=20$ cm. (c) $z=30$ cm, (d) $z=40$ cm. (e) $z=50$ cm.

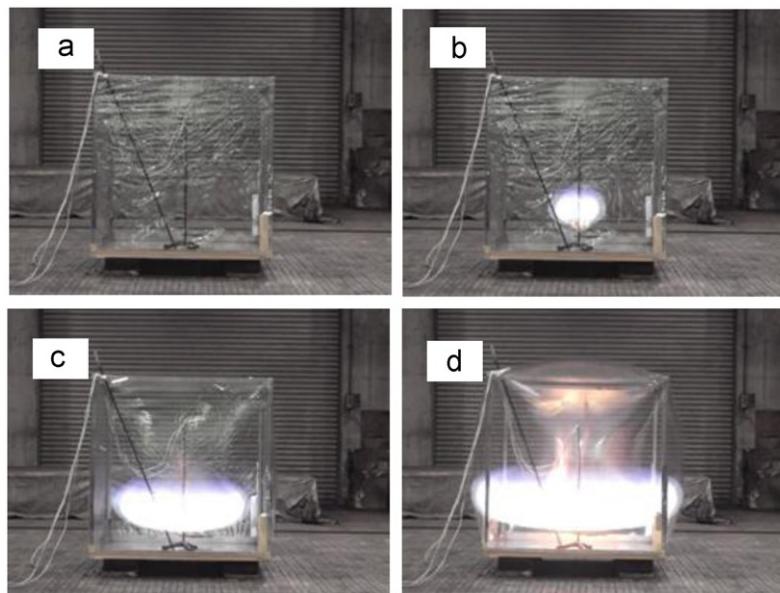


Fig. 17. Combustion behavior of flammable mixture from a fuel spill on a floor in a frame vessel. ($h_i=20$ cm, $t_i=30$ min). (a) $t=0$ s. (b) $t=100$ ms. (c) $t=200$ ms. (d) $t=300$ ms.

mixture was assumed to be from 1.4 to 7.6 vol% as well as that of gasoline vapor-air mixture [14], and the possibility of ignition was predicted. The evaporation and diffusion model were verified by the

Table 4
Results of ignition experiments and ignition predictions.

	Ignition height h_i (cm)			
	5	10	20	30
40	×	×	×	×
	× (0%)	× (0%)	× (0.2%)	× (0.6%)
30	×	×	×	×
	× (0%)	× (0.1%)	× (0.9%)	○ (1.8%)
20	×	○	○	○
	× (0.2%)	○ (1.4%)	○ (3.3%)	○ (1.8%)
10	○	×	×	×
	○ (4.0%)	○ (6.5%)	× (7.9%)	× (8.1%)

Upper row: results of ignition experiments.

Lower row: ignition predictions (predicted concentration of fuel vapor).

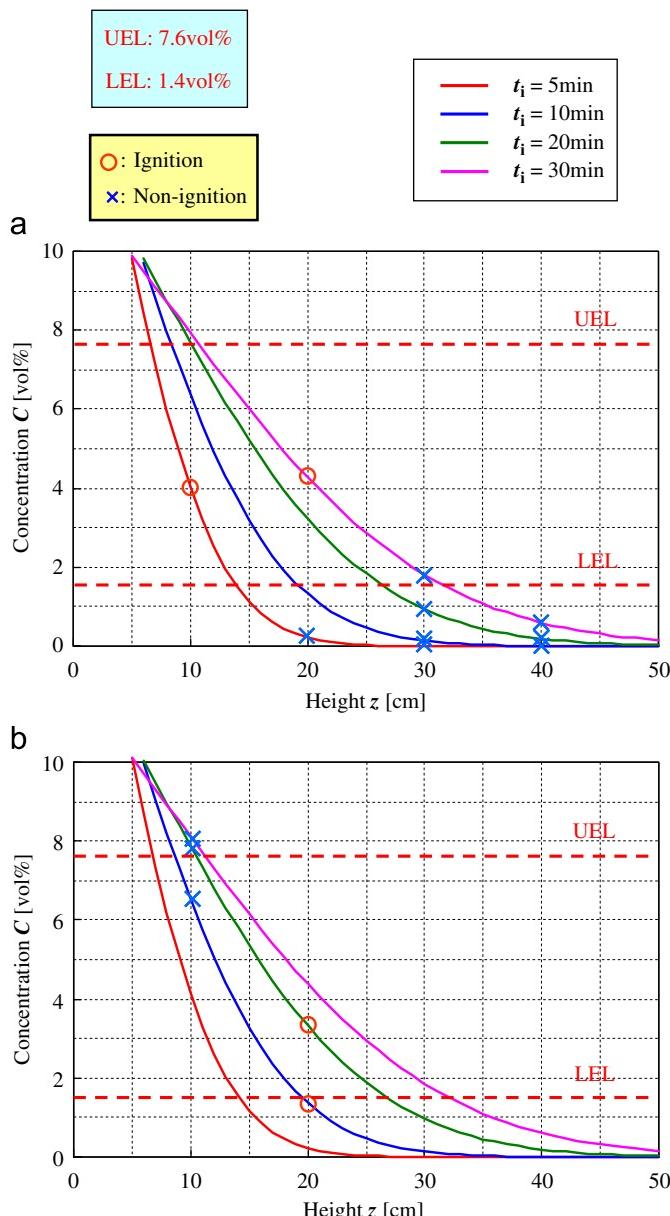


Fig. 18. Results of Ignition experiments and predicted concentration of vapor from mixed fuel spill on a floor. (a) $T=23\text{ }^{\circ}\text{C}$. (b) $T=24\text{ }^{\circ}\text{C}$.

comparison of the results of ignition experiments with the ignition predictions. The experimental results and ignition predictions are shown in Table 4, and the predicted vapor concentrations with the experimental results are shown in Fig. 18. The experimental results at 20 and 40 cm height agreed with the ignition predictions by the calculated concentration. The calculated vapor concentrations at 10 cm height in 10 min and at 30 cm height in 30 min were within the flammable range; nevertheless, ignition was not observed in the corresponding experiments. The calculated vapor concentrations in these conditions were close to the flammable limit, therefore, the experimental errors, such as the liquid temperature change by the latent heat of evaporation and the turbulence diffusion when the fuel was poured on the vessel base, were expected to cause the difference between the prediction and experimental results. While the fuel mixtures were multi-component, the molecular weight, diffusion constant and flammable range were assumed to the specific values. It was supposed that the assumption was also a factor that caused the different.

Thus, it was confirmed that the range where the flammable mixture is formed can be well predicted by calculating the vapor concentration distribution of fuel mixtures using the presented evaporation and diffusion model. The fire hazard in the cases where a fuel mixture of gasoline and kerosene in an arbitrary mixture ratio is spilt on a floor could be estimated by the presented model.

4. Conclusion

The aim of this paper is to accurately predict the evaporation and diffusion behavior of fuel mixtures of gasoline and kerosene in an arbitrary mixture ratio. The evaporation characteristics of fuel mixtures and concentration distributions of vapor from a fuel mixture spill on a floor were measured. The evaporation model assuming fuel mixture as two-component liquid of gasoline and kerosene was presented. The vapor pressures, the flash points and the evaporation rates of fuel mixtures were predicted by using the model. The calculated values were compared with the measured values, and the change in the evaporation characteristics of fuel mixtures by evaporation was investigated quantitatively. The calculated values of vapor pressures, flash points and evaporation rates corresponded to the measured values; therefore, it was confirmed that the change in the evaporation characteristics by evaporation can be predicted by the presented model.

The diffusion model above a fuel mixture spill on a floor based on the unidimensional diffusion equation [7] was prepared, and the method for predicting a concentration distribution of flammable vapor generated from a fuel mixture of gasoline and kerosene in an arbitrary mixture ratio was presented. The calculated vapor concentrations agreed well with the measured results. Experiments to ignite the vapor above a fuel mixture spill on the base plate of the frame vessel were carried out, and the existence of the ignition by a spark discharge generated in various elapsed times at various heights was observed. The experimental results agreed well with the ignition predictions by the calculated concentration. From these results, it was confirmed that the range where the flammable mixture is formed can be well predicted using the presented evaporation and diffusion model.

Gasoline and kerosene are multi-component fuel mixture and the physical properties differ with each product. In order to predict evaporation and diffusion behaviors of fuel mixtures accurately, it is most desirable to get the parameters of evaporation characteristics, $\alpha_A, \alpha_B, \beta_A, \beta_B$ and k in each case. However, the evaporation and diffusion behavior of vapor from a fuel mixture spill on a floor can be predicted approximately using the parameters presented in Table 1 because the vapor pressure of

gasoline is defined within 44–78 kPa at 38 °C by the standard of fuels (JIS K 2202). The method presented in this paper can provide useful information to estimate the fire hazard in the cases where a fuel mixture of gasoline and kerosene in an arbitrary mixture ratio is spilt on a floor.

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